Polyaromatic Naphthalene Derivatives as Heat Transfer Fluids

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CONCENTRATING SOLAR POWER: RECEIVERS

CSP collectors are now limited to temperatures <400°C

- *Issues are fluid stability, vapor pressures, materials compatibility*
- *Higher temperatures allow better thermodynamic efficiency*
- *Substituted naphthalenes have enhanced thermal stability, permitting repeated cycling.*
- *Desirable thermophysical properties such as low vapor pressures, and low melting points.*
- *Project scope included*
  - *Evaluation of synthesis, thermal performance, materials interactions*
  - *Currently testing in high temperature loop*
  - *Pilot scale loop tests planned for end of 2012*

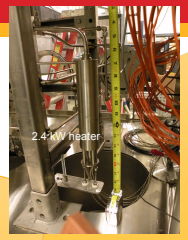
Suzuki Cost Analysis

Reagent	Amount used (g)	Cost $/gram	Percent of total	Comments
1-bromonaphthalene	1221	0.378	38.6	Other Supplier s~ 50.244/gram
Phenylboronic acid	750	0.35	22	
Pd(II)acetate	4.14	50	17.3	Polymer support, recyclable catalyst Reduce catalyst loading
Tri-o-tolylphosphine	16.3	8.32	11.3	
Potassium carbonate	975	0.05	4.1	
n-propanol	5 L	16 (per Liter)	6.7	Recycle solvent (azeotropes w/ water)
Total		$1200/Liter		

Other possibilities for process development
- Reduce catalyst loading
- Recyclable catalyst –
  - Eliminates need for phosphine
  - Would break even after ~4 uses.
- Continuous flow reactor

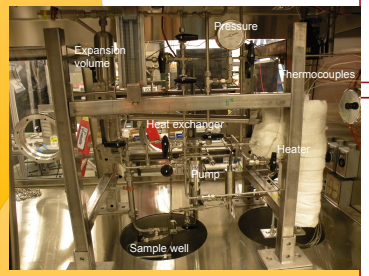
Kumada Coupling Alternative

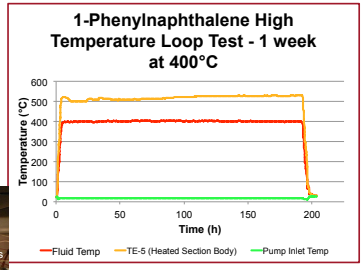
Reagent	Amount used (g)	Cost $/gram	Percent of total	Comments
1-chloronaphthalene (tech grade 85%, remainder 2- isomer)	1128	0.19	37	
Phenylmagnesium Bromide	1115	.153	30	Based on 18L semibulk at $-A (3.0 M in diethyl ether) Could be generated in situ from bromobenzene and Mg (EXOTHERMIC!)
Bis (triphenylphosphine)Ni(II)chloride	4.0	2.2	1.5	
Diethyl ether	5L	180/5L	31	Can be recovered and recycled.
Total		$574/Liter		

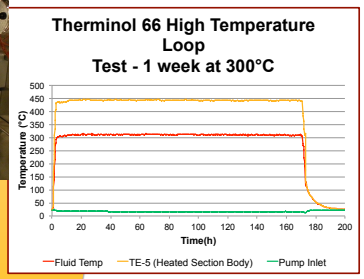


High Temperature Loop Tests

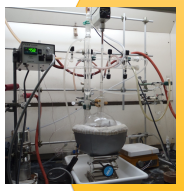
- 4x600 W cartridge heaters
- 1 mL/min and up – variable pump speed
- 0.7- 1 L fluid capacity
- Pressure to 8 bar
- Stainless steel throughout except viton o-rings on pump (cold side)
- 2 heat exchangers
- Variable cooling water temperature





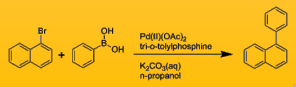


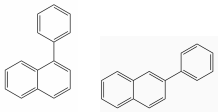
Synthetic Pathways



Scale up to batches of several hundred mL

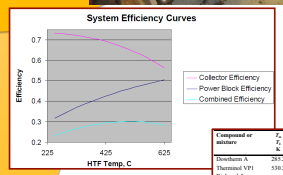
Suzuki Coupling gives high yields.





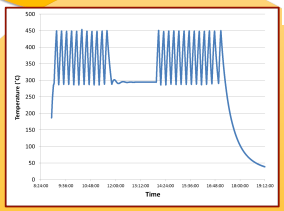
Pilot-Scale Loop

- Cool Energy Inc
- Rooftop assemby in Boulder CO
- Coupled Stirling engines to generate power
- Moderate temperatures, to 325°C
- 120 L volume of fluid



Stability Tests

Ramping Test Temperature Profile



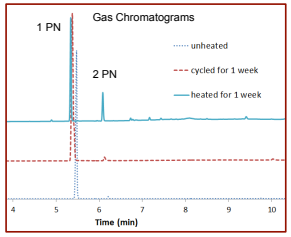
- 1 mL samples of fluids in 4 or 7 mL sealed vessels
- Heating periods from 1 week to 1 month
- Fluids: 1-phenylnaphthalene, alone and with fluoranthene
- Contact with coupons of stainless steel, brass, carbon steel
- PID control of heater for unattended operation
- Analysis by gas chromatography (mass spectroscopic and flame ionization detection) and nuclear magnetic resonance
- Static tests to 500°C and ramping from 290 to 450°C

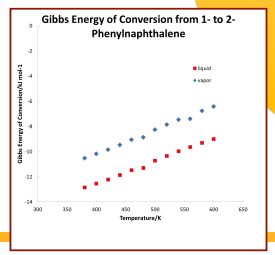
LCOE Analysis

- NREL Solar Advisory Model
- High Efficiency Collector
- Best efficiency for trough system when peak temperature ~ 475°C
- Modest gains in LCOE for modified fluid only
- Reduction of 4-5 ¢ / kWh when coupled with thermal energy storage

Comparison of Thermal Fluids

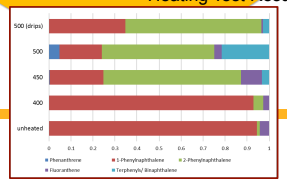
Compound or mixture	T_m / T_f K	C_p kJ·kg^{-1}·K^{-1}	Liquid kg·m^{-3}	T_c (K) P_c (bar)	Vapor Press. bar	Liquid W·m^{-1}·K^{-1}	Liquid mPa·s
Dowtherm A	285.2	2.19	788	770±1	1.8	0.0911	0.29
Therminol VP1	530.2	*2.725*	*672.5*	32.2±0.9	*11.32*	*0.0771*	*0.12*
Biphenyl & diphenyl oxides @ 600 K @ 673 K (Max)							
Xcelthern 600-C_{30} paraffin oil @ 588.8 K	T_m range 574–741	3.001	672.36	768 ±0.7	0.2499	0.1122	0.252
H_2O @563 K, 7.5 MPa	273.15 – 373.1	5.5	732	646.95 220.64	Super-heated	0.56	0.13
Biphenyl @ 500 K	342 – 559	2.03	869	773±3 33.8±1	0.531	0.118	0.32
o-Terphenyl @ 500 K	485 – 623	1.98	947	800±10 29.9±6	0.0199	0.135	0.75
Therminol 66 Mix of hydrogenated terphenyls @ 600 K @18 K (Max)	266 – 652	2.67	786	842 24.3	0.542	0.0911	0.359
1-phenylnaphthalene @ 600K	T_m range 297–318 598	2.6	849	818 7.1	0.820	0.077	0.11

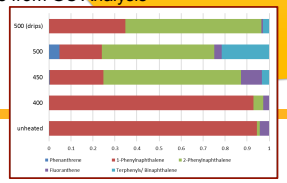




The 2-phenyl is more stable than the 1-phenyl as calculated using thermophysical property data.

Heating Test Results from GC Analysis





SunShot U.S. Department of Energy

www.solar.energy.gov/sunshot/csp.html